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TITLE OF INVENTION

FINE PARTICLE OF POLYMER FOR PLASTISOL AND MANUFACTURING PROCESS THEREFOR AS WELL AS NON-HALOGENATED PLASTISOL COMPOSITION AND ARTICLE PRODUCED THEREFROM

APPLICANT(S) FOR DO/EO/US

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Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Request for Consideration of Documents Cited in International Search Report/Request for Priority

PCT/IB/304

PCT/IB/308

DESCRIPTION

Fine particle of polymer for plastisol and
manufacturing process therefor as well as
non-halogenated plastisol composition and
5 article produced therefrom

Technical Field

This invention relates to a fine particle of
polymer which allows a non-halogenated plastisol to be
10 prepared with a small amount of a plasticizer and a
manufacturing process therefor, as well as a non-
halogenated plastisol composition and an article
produced therefrom. This invention also relates to a
non-halogenated plastisol composition having viscosity
15 properties for good workability, exhibiting good
suitability to processing into an airless spray and
suitable as a coating or sealing material.

Background Art

20 A plastisol in which a fine particle of polymer is
dispersed in a plasticizer as a medium has been
utilized in a variety of industrial applications, but a
vinyl-chloride plastisol (hereinafter, referred to as
"PVC sol") using a polyvinyl chloride is used in most
25 of these applications. Owing to their good
processability and physical properties, PVC sols have

been used in a wide variety of applications such as wallpapers, undercoats for an automobile, body sealers for an automobile, carpet backing materials, floor materials, paints and toys, and thus industrially carries significant value.

Besides many properties such as strength after curing by heating, elongation, rubber elasticity, flexibility, low-temperature properties and damping, a PVC sol exhibits good workability in a sol state before curing by heating and good processability.

"Good workability" as used herein means that a relatively smaller amount of a plasticizer may be combined to a fine particle of polymer and that a resulting sol has a lower viscosity so that it may be easily introduced in a variety of processing lines. In other words, to a certain amount of a plasticizer, a larger amount of an inorganic filler may be added. Such a plastisol which can be formed with a small amount of a plasticizer permits freedom in compounding, may be easily introduced in a processing line and can be widely applied regardless to an application.

The fact that a small amount of a plasticizer may be combined with a fine particle of polymer considerably contributes for improving not only workability but also physical properties of a molding. For example, a smaller amount of a plasticizer in a

molding may prevent bleed-out of the plasticizer with time and may improve strength or an elastic modulus of a molding.

However, a PVC sol or an article prepared therefrom generates hydrogen chloride gas during incineration, which is believed to cause problems in relation to the environment and an incinerator such as considerable damage to the incinerator and acid rain due to hydrogen chloride gas discharged to the air.

More recently, the gas has been believed to be one of causes generating extremely poisonous substances such as dioxins. There has been, therefore, needs for developing an alternative material because of strong concern about adverse affect to a human body or the global environment.

Such environmental problems are associated with not only a PVC sol but also a plastisol using a halogen-containing polymer in general. It has been, therefore, desired to develop a plastisol using a polymer without halogen atoms, i.e., a non-halogenated plastisol. As one candidate, an acrylic plastisol using an acrylic polymer (generally called an "acrylic sol") has been proposed.

There have been proposed procedures for reducing the content of chlorine atoms in order to solve the above problems in a PVC sol. For example, JP-As 60-

258241, 61-185518 and 61-207418 have proposed an attempt that a complex is formed from vinyl chloride and another polymer material such as an acrylic polymer to provide a plastisol with a reduced chlorine content.

5 Although the halogen content is reduced in such a plastisol, it still contains halogen atoms. Thus, the problem of generation of hydrogen chloride gas or dioxins during incineration has not been essentially solved.

10 JP-As 7-233299 and 8-295850 have proposed a plastisol using a particulate acrylic polymer, i.e, an acrylic sol as a non-halogenated plastisol with no halogen atoms.

15 Generally an acrylic sol has a quite similar appearance to a PVC sol, but the former has considerably different properties of a fine particle of polymer and therefore quite different workability or processability. For example, even when an acrylic sol and a PVC sol are prepared as a fine particle of
20 polymer having the same particle size and size distribution, they exhibits considerably different viscosity, thixotropic properties and leveling properties. Therefore, in developing an acrylic sol or an article therefrom, an acrylic sol with desired
25 properties cannot be obtained when employing known technique and information for a PVC sol as such.

These publications have disclosed an acrylic sol just for proposing a non-halogenated plastisol as an alternative material to a PVC sol. Its workability is significantly lower than that for a PVC sol.

5 For example, in the acrylic sol described in the publications, the lower limit of a plasticizer required for solation is considerably higher and a resulting plastisol has a higher viscosity so that it cannot be easily introduced in an existing processing line, i.e,
10 reduced workability; a molding cannot be quickly formed in a short period; and a resulting article exhibits lower strength, i.e., reduced processability. A relatively higher amount of a plasticizer may leads to its bleed-out with time from the resulting article.
15 Furthermore, a sol viscosity increases at a higher rate so that the sol has a shorter shelf life and a shorter working life.

In terms of workability in spray coating using, for example, an airless spray, an acrylic sol proposed
20 in the previous publications cannot provide viscosity properties required for spray coating. In particular, it cannot be used for an application involving an airless-spray coating such as an undercoat or body sealer for an automobile.

25 For example, JP-A 8-3411 has described that an acrylic sol disclosed therein can provide a low-

viscosity sol whereby uneven coating may be prevented. It, however, has a too high viscosity to be used in an airless spray. When adding a large amount of a plasticizer for reducing a viscosity, a coated sol may generate sagging so that an adequate film thickness or coating pattern cannot be maintained. When a reduced amount of a plasticizer is added to increase a viscosity for avoiding sagging, sagging can be prevented while airless-spray coating itself cannot be conducted due to an excessively higher viscosity. Thus, the prior art has not provided an acrylic sol having viscosity properties required for airless-spray coating.

There have been no descriptions of a non-halogenated plastisol without halogen atoms which generate toxic materials such as hydrogen chloride and dioxins during incineration and exhibiting good workability and processability.

Disclosure of the Invention

An objective of this invention is to provide a fine particle of polymer whereby a non-halogenated plastisol can be prepared with adding a small amount of a plasticizer, a non-halogenated plastisol composition using the particles, and an article prepared using the particles. Another objective of this invention is to provide a non-halogenated plastisol composition with

viscosity properties giving good workability, having good processing suitability to an airless spray and suitable to a coating or sealing material.

5 This invention relates to a fine particle of polymer for a plastisol free from halogen atoms and having a specific surface area of 0.6 to 20.0 m²/g as determined by nitrogen-gas adsorption.

10 This invention also relates to a process for manufacturing a fine particle of polymer for the above plastisol, comprising the steps of preparing an aqueous dispersion of a fine particle of polymer in which primary particles have an average particle size of at least 500 nm; drying the aqueous dispersion at not lower than 50 °C but not higher than [a glass-
15 transition temperature of the polymer + 20] °C, by spray drying.

This invention also relates to a non-halogenated plastisol composition containing the above fine particle of polymer for a plastisol and a plasticizer.

20 This invention also relates to a non-halogenated plastisol composition comprising the above particulate acrylic polymer for a plastisol consisting of agglomerates formed from a plurality of primary particles in which the primary particles have an
25 average particle size of at least 500 nm; a plasticizer; and an organic filler.

This invention also relates to a coating material consisting of the above plastisol composition.

This invention also relates to a sealant consisting of the above plastisol composition.

5 This invention also relates to an article produced using the plastisol composition.

 A fine particle of polymer for a plastisol of this invention, a non-halogenated plastisol composition using the particles and an article therefrom do not
10 generate toxic substances such as hydrogen chloride gas and dioxins during incineration because they do not contain halogen atoms.

 According to this invention, a non-halogenated plastisol composition with lower viscosity exhibiting
15 good workability and processability can be provided by adding only a small amount of a plasticizer. In particular, this invention may provide a non-halogenated plastisol composition exhibiting good processing suitability into an airless spray and
20 suitable as a coating material or sealant.

 Thus, this invention carries remarkable industrial significance and considerably effects on global environmental protection.

25 Best Mode for Carrying Out the Invention

 We have intensely attempted to achieve the above

objectives and have finally found that it is necessary to control a specific surface area of a fine particle of polymer used within a particular range for providing a plastisol which can be compounded with a small amount
5 of a plasticizer, i.e., good workability, and can rapidly provide a molding by heating for a short time, i.e., good processability.

Specifically, we have found that compared with polyvinyl-chloride particles used in a PVC sol, a
10 conventional particulate acrylic polymer used in an acrylic sol may be characterized in that i) they have a large area contacting with a plasticizer due to their excessively large specific surface area, ii) on the contrary, they have a small area contacting with a
15 plasticized due to their excessively small specific surface area, or iii) they absorb a large amount of oil so that most of a plasticizer may be absorbed in the fine particle of polymer, and that these properties cause the problems in workability and processability.

20 Then, we have investigated the problems and have found that a particulate non-halogenated polymer having a specific surface area of 0.6 to 20.0 m²/g as determined by nitrogen-gas adsorption can be used to provide non-halogenated plastisol composition with good
25 workability and processability, resulting in this invention.

In terms of processing suitability to spray coating such as an airless spray, we have found that viscosity properties of a sol, i.e., a high-shear viscosity and a low-shear viscosity, may be adjusted to
5 a particular range to achieve good suitability, resulting in this invention. This invention will be described in detail.

Although an acrylic sol as one of non-halogenated plastisols have the same appearance as a PVC sol, i.e.,
10 it is a sol in which a fine particle of polymer is dispersed in an organic medium (a plasticizer), the acrylic sol employs resins exhibiting essentially different properties as a fine particle of polymer. Thus, when the prior art for a PVC sol is simply
15 applied to an acrylic sol, some properties such as viscosity properties becomes quite different so that good properties in workability and processability cannot be obtained as in a conventional manner.

Specifically, for a PVC sol there is strong
20 intermolecular cohesive force in a fine particle of polymer so that it exhibits good storage stability in the presence of a plasticizer irrespective of a polymer particle size or molecular weight, while for an acrylic sol, there is not such strong intermolecular cohesive
25 force so that storage stability is usually lower in the presence of a plasticizer.

Wettability to a plasticizer is different between a PVC sol and an acrylic sol, so that they exhibit significantly different dispersion in the plasticizer, i.e., showing quite different viscosity behavior of a sol. For example, in order to reduce a sol viscosity, a known technique of adding a viscosity-reducing agent such as an emulsifier or dispersant may be used for a PVC sol, whereas such a technique may not be necessarily effective for an acrylic sol. Furthermore, for a particle size distribution for a fine particle of polymer, a particle size distribution most optimal to a PVC sol may not necessarily provide similar properties when applied to an acrylic sol.

As described above, it is difficult to achieve desired properties by simply applying techniques for a PVC sol to a non-halogenated plastisol. For providing a non-halogenated plastisol having desired properties, it is thus necessary to employ the following particular configuration.

A fine particle of polymer for a plastisol of this invention must be comprised of a non-halogenated polymer containing no halogen atoms for avoiding generation of toxic substances derived from halogen atoms such as hydrogen chloride and dioxins. A preferred non-halogenated polymer is an acrylic polymer. An acrylic polymer has advantages that i) a polymer

having a desired higher polymerization degree can be easily obtained by radical polymerization, ii) fine particles can be easily obtained by a technique such as emulsion polymerization and suspension polymerization, 5 iii) a polymerization composition can be easily optimized because a monomer can be selected from a wide variety of co-polymerization monomers, and iv) reactivity or properties such as adhesiveness to a base material can be easily endowed because a variety of 10 functional groups may be introduced in a polymer.

A fine particle of polymer for a plastisol of this invention must have a specific surface area of 0.6 to 20.0 m²/g as determined by nitrogen gas adsorption.

The amount of a plasticizer for providing a 15 plastisol may depend on many factors, but in particular, a contact area of a fine particle of polymer with a plasticizer, i.e., a specific surface area of a fine particle of polymer, is most significant.

In contrast with a polyvinyl chloride having 20 strong intermolecular cohesive force, a non-halogenated polymer, in particular, an acrylic polymer, gradually swells by absorbing a plasticizer with time so that a viscosity of a plastisol gradually increases, leading to reduction in storage stability in a remarkable case.

25 Furthermore, an absorption rate for a plasticizer depends on compatibility between a polymer and a

plasticizer. These are influenced by a contact area of a fine particle of polymer with a plasticizer. In other words, it is necessary for reducing an absorption rate for a plasticizer that a specific surface area of a fine particle of polymer is small.

On the other hand, it is desired for processability when a plastisol is cured by heating that a polymer swells and is dissolved by rapidly absorbing a plasticizer by heating for a short period. In this respect, it is necessary that a contact area with a plasticizer, i.e., a specific surface area is large.

As described above, a specific surface area of a fine particle of polymer significantly influences workability related to the amount of a plasticizer and storage stability and processability, i.e., curing by heating for a short period. It is, therefore, necessary to control a specific surface area of a fine particle of polymer to 0.6 to 20.0 m²/g.

Controlling a specific surface area of a fine particle of polymer to 0.6 to 20.0 m²/g allows workability or processability to be improved even when using a non-halogenated polymer with a relatively weak intermolecular cohesive force.

A specific surface area of a fine particle of polymer exceeding 20.0 m²/g may make an absorption rate

of a plasticizer so high that the polymer may considerably swell in a short time. Although it is preferable in that a process of curing by heating can be short, it may result in problems that a large amount of a plasticizer is required for compounding so that the system becomes of a higher viscosity and that a viscosity-increasing rate of a plastisol composition with time may be so high that a working life is reduced, leading to reduction in workability.

When a specific surface area of a fine particle of polymer is less than $0.6 \text{ m}^2/\text{g}$, a contact area with a plasticizer becomes so small that a plasticizer-absorption rate of a fine particle of polymer is significantly reduced during a process of curing by heating. Thus, gelling or molding cannot adequately proceed by heating for a short time so that a strong molding cannot be obtained, leading to reduction in processability.

In this invention, a more preferable range of a specific surface area of a fine particle of polymer is 1.0 to $10.0 \text{ m}^2/\text{g}$. A specific surface area within this range may provide advantages that a very small amount of a plasticizer may be adequate for compounding and that a resulting plastisol may exhibit a significantly reduced viscosity, while it may allow satisfactory molding to be performed in a short period during a

process of curing by heating and may provide a plastisol composition with desired properties.

As described above, a specific surface area of a fine particle of polymer is one of significant factors for obtaining desired properties for a plastisol. An oil absorption rate of a fine particle of polymer is also an important factor. Specifically, when adding a certain amount of a plasticizer is added to fine particles of polymer with different oil absorption rates, a fine particle of polymer with a lower oil absorption rate may provide a plastisol with a lower viscosity.

We have thus investigated a suitable range of an oil absorption rate for a fine particle of polymer for a plastisol and have found that as determined for linseed oil, a preferable range of an oil absorption rate is up to 0.8 mL/g (cc/g). Using a fine particle of polymer having an oil absorption rate within this range, a viscosity can be considerably reduced in comparison with a conventionally proposed acrylic plastisol, resulting in good workability irrespective of an application.

A specific surface area and an oil absorption rate are apparently, but not actually, correlated with a particle size of a fine particle of polymer. For a non-halogenated plastisol proposed in previous

publications, there have been many proposals in which a particle size of a fine particle of polymer is restricted, but we have found after investigation that restriction to a particle size cannot always improve
5 workability or processability.

A fine particle of polymer used in a plastisol has a form of two- or more dimensional agglomerates of many primary polymer particles. Therefore, even particles with an equal particle size may exhibit a significantly
10 different specific surface area or oil absorption rate. In other words, there is not correlation between a particle size and a specific surface area and thus simply defining a particle size as in previous proposals cannot essentially solve the problems. In
15 fact, even when using a preferable polymer particle size proposed in the previous publications, a plastisol with an adequately low viscosity cannot be sometimes provided. In contrast, according to this invention using a fine particle of polymer with a particular
20 specific surface area, a plastisol composition with a lower viscosity can be provided.

Among factors determining an aggregation state of primary particles in an agglomeration structure of a fine particle of polymer, a particularly influential
25 factor is a drying temperature during preparing a fine particle of polymer. Although it cannot be generally

defined because a polymer composition or a glass-
transition temperature must be taken into account, a
specific surface area tends to be reduced by drying at
an elevated temperature while it tends to be increased
5 by drying at a lower temperature. Besides a drying
temperature, a specific surface area of a fine particle
of polymer depends on, in a complex manner, many
factors such as a primary particle size, a glass-
transition temperature of the polymer, a surface state
10 of the primary particles and a particle structure.
Therefore, the problems cannot be essentially solved
only by defining a particle size, and a practical level
of workability or processability can be achieved only
by selecting a specific surface area within a
15 particular range as in this invention.

The term "workability" practically carries more or
less different meanings depending on a processing
method used. It may be common in any case that a
smaller amount of a plasticizer required for a
20 plastisol may lead to higher freedom in compounding, to
a lower viscosity of a resulting plastisol, and thus to
good workability.

A processing method for a plastisol depends on an
application so that some modification is needed for
25 each processing method. Such modification are
generally achieved by optimizing viscosity properties

depending on a shear speed on a plastisol.

For example, an article to be coated is immersed in a plastisol and then drawn up in dip coating so that the a high shear speed is not applied to the plastisol.

5 It is, therefore, preferable herein that a viscosity is low under a low shear speed.

In another case, e.g., a wallpaper or cloth prepared by calendar processing, a plastisol is coated on a line operated at a higher speed so that a
10 relatively higher shear speed is applied to the plastisol. It is, therefore, preferable herein that a viscosity is low under a relatively higher shear speed.

For airless-spray coating, a plastisol is sprayed as a mist from a nozzle by applying a very high
15 pressure to the plastisol for coating so that a very high shear speed is applied to the plastisol. It is, therefore, preferable herein that a viscosity is low under a very high shear speed.

In any case, it is necessary to define a specific
20 surface area of a fine particle of polymer within the above particular range. Other materials such as inorganic fillers with a variety of attributes can be added to the plastisol to adjust a viscosity to a desired level under a given shear speed.

25 A fine particle of polymer for a plastisol of this invention is made of a non-halogenated polymer

containing no halogen atoms such as acrylic polymers,
styrene polymers, butadiene polymers and vinyl-acetate
polymers as well as their copolymers including styrene-
butadiene copolymers, acrylonitrile-butadiene
5 copolymers and acryl-vinyl acetate copolymers.

These polymers can be selected depending on an
application. For example, a styrene-butadiene
copolymer may be used when a higher rubber elasticity
is required while an acryl-vinyl acetate copolymer may
10 be used when higher compatibility to a plasticizer is
needed.

An acrylic polymer is preferably used in a fine
particle of polymer for a plastisol of this invention.
A more preferable acrylic polymer is that comprising at
15 least 50 mol% of an alkyl methacrylate and/or an alkyl
acrylate (hereinafter, referred to as an "alkyl
(meth)acrylate" as appropriate) as a constituent
monomer. That is, a polymer containing at least 50
mol% of an alkyl (meth)acrylate unit is preferable.

20 Since among monomers giving a non-halogenated
polymer, an alkyl (meth)acrylate has quite many
variations, it may be used to easily prepare a
copolymer having a desired glass-transition temperature
and solubility parameters in a wide range.

25 Such an acrylic polymer may be, therefore, used as
a fine particle of polymer for a plastisol to control

compatibility between the fine particle of polymer and a plasticizer within a desired range and to facilitate compatibility between storage stability and plasticity retention after deposition or molding which are
5 important for a plastisol.

A glass-transition temperature of a polymer constituting a fine particle of polymer may be appropriately adjusted to provide a coating film or molding having a hardness, a strength, an elongation
10 and an elastic modulus depending on an application.

When an alkyl (meth)acrylate unit is contained to a level of 50 mol% or more in a polymer constituting a fine particle of polymer, the properties of an acrylic polymer as described above can be easily achieved and
15 improve freedom in designing a polymer for a plastisol.

Examples of the above alkyl (meth)acrylate includes (meth)acrylates of a linear alkyl alcohol such as methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, i-butyl (meth)acrylate, t-butyl
20 (meth)acrylate, hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate and octyl (meth)acrylate; and (meth)acrylates of a circular alkyl alcohol such as cyclohexyl (meth)acrylate.

Among these, preferable examples include methyl
25 (meth)acrylate, n-butyl (meth)acrylate, i-butyl (meth)acrylate, t-butyl (meth)acrylate and 2-ethylhexyl

(meth)acrylate. These monomers are readily available and are suitable to industrial practical use. This invention is, however, not limited to these specific monomers.

5 Examples of other monomers which may be used include carboxyl-containing monomers such as methacrylic acid, acrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, 2-succinoyloxyethyl methacrylate-2-methacryloyloxyethylsuccinic acid, 2-
10 maleinoyloxyethyl methacrylate-2-methacryloyloxyethylmaleic acid, 2-phthaloyloxyethyl methacrylate-2-methacryloyloxyethylphthalic acid and 2-hexahydrophthaloyloxyethyl methacrylate-2-methacryloyloxyethylhexahydrophthalic acid; sulfonic-
15 containing monomers such as allylsulfonic acid; carbonyl-containing (meth)acrylates such as acetoacetoxyethyl (meth)acrylate; hydroxy-containing (meth)acrylates such as 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate; epoxy-containing
20 (meth)acrylates such as glycidyl (meth)acrylate; amino-containing (meth)acrylates such as N-dimethylaminoethyl (meth)acrylate and N-diethylaminoethyl (meth)acrylate; polyfunctional (meth)acrylates such as (poly)ethyleneglycol di(meth)acrylate, propyleneglycol
25 di(meth)acrylate, 1,6-hexanediol di(meth)acrylate and trimethylolpropane tri(meth)acrylate; acrylamides and

their derivatives such as diacetoneacrylamide, N-methylolacrylamide, N-methoxymethylacrylamide, N-ethoxymethylacrylamide and N-butoxymethylacrylamide; styrene and their derivatives; vinyl acetate; urethane-
5 modified acrylates; epoxy-modified acrylates; and silicone-modified acrylates. These can be extensively used and can be selected depending on an application.

A fine particle of polymer for a plastisol of this invention preferably has two or more polymer layers
10 having different compositions concentrically from the particle center to its surface.

A polyvinyl chloride has a strong intermolecular cohesive force so that a plasticizer infiltrates at a lower rate and thus a plastisol composition exhibits
15 good storage stability without using a concentric multilayer particle structure as described above. On the other hand, a non-halogenated polymer such as an acrylic polymer generally has a weak intermolecular cohesive force so that a plasticizer can easily
20 infiltrate. Infiltration of the plasticizer may be delayed by forming a particle structure having two or more polymer layers concentrically from the particle center to the surface, using polymer components having different compositions as described above. In this
25 manner, properties such as storage stability, property of curing by heating and plasticizer retention may be

improved even when using a particulate non-halogenated polymer.

Examples of such a particle structure include a core shell type structure consisting of two layer of a core polymer and a shell polymer; a multi-step layer type structure consisting of three or more layers; and a gradient type structure having a semi-continuous composition variation using very thin layers. Among these, a core shell type of particle structure is, but not limited to, preferable in the light of easy preparation of a fine particle of polymer.

In such particle structures, it is preferable that compatibility of a polymer to a plasticizer in an inner layer close to the center is higher than that in an outer layer close to a particle surface. Such a configuration may improve storage stability of a plastisol, accelerate swelling and dissolution of a fine particle of polymer by a plasticizer during heating, and prevent bleed-out of the plasticizer after deposition or molding.

A fine particle of polymer for a plastisol may be prepared an appropriate polymerization technique such as emulsion polymerization, seed emulsion polymerization, soap-free emulsion polymerization, suspension polymerization and fine suspension polymerization. When a medium is not aqueous,

dispersion polymerization in an organic medium or in a mixture of water and an organic medium or precipitation polymerization in an organic medium may be employed. A complex polymerization technique combining a plurality of these polymerization methods may be, if necessary, used.

In particular, for preparing a fine particle of polymer having a core shell type, multi-step layer type or gradient type particle structure, it is practical to use, among these methods, emulsion polymerization, seed emulsion polymerization or soap-free polymerization in an aqueous medium in the light of controllability of a particle structure and a higher polymer molecular weight obtained which may improve physical properties of a coating film or molding. For preparing primary particles with a relatively larger size, soap-free emulsion polymerization and fine suspension polymerization are preferable.

Since a fine particle of polymer prepared by any of these polymerization methods is generally obtained as a dispersion in which the particles are dispersed in a medium, a step of recovering a fine particle of polymer from a polymer dispersion is necessary. This recovery process may be conducted by any appropriate known technique such as spray drying, coagulation, freeze drying, centrifugation and filtration. Among

these, spray drying is better because of controllability of particle properties and a higher yield.

For a fine particle of polymer of this invention, there are no restrictions to their secondary or higher structure as long as a specific surface area is within a range of 0.6 to 20.0 m²/g. For example, the particles may have a secondary-particle structure of secondary particles consisting of primary particles aggregated by a weak cohesive force, secondary particles consisting of primary particles aggregated by a strong cohesive force or secondary particles mutually fused by heating. Alternatively, a higher-order structure may be formed by treatment (e.g., granulation) of these secondary particles.

These higher-order particle structures may be appropriately designed depending on an application or its requirements. For example, they may be designed for improving workability such as controlling powdering and flowability improvement or for improving physical properties such as modification of a dispersion state of a fine particle of polymer to a plasticizer.

A fine particle of polymer for a plastisol of this invention preferably has an average particle size of 500 nm or more in their primary particles constituting secondary or higher particles. A specific surface area

of a polymer particle cannot be simply determined by a primary particle size because it is influenced in a complex manner not only by a primary particle size but also many factors such as a size distribution, a degree of fusion among primary particles and a secondary or higher structure. However, when primary particles have an average particle size of 500 nm or more, it is easy to control a specific surface area of a fine particle of polymer within a desired range by adjusting the other factors. Furthermore, it is preferable that an average particle size of primary particles is 10 μm or less for quickly conducting melting, deposition or molding for a short period.

A fine particle of polymer for a plastisol of this invention having a particular specific surface area may be prepared by any of the following methods.

a) A dispersion of a polymer having a relatively larger primary particle size is prepared and it is then dried under the conditions whereby heat fusion among particles occurs to a lower level.

b) A dispersion of a polymer having a relatively smaller primary particle size is prepared and it is then dried under the conditions whereby heat fusion among particles occurs to a higher level.

c) A dispersion of a polymer having a relatively larger primary particle size and having fine pores on a

particle surface is prepared and it is then dried under the conditions whereby heat fusion among particles occurs to a lower level.

- d) A dispersion of a polymer having a relatively larger primary particle size is prepared; to the dispersion is added a binder component which can be easily fused by heating; and the mixture is then dried.

For preparing a fine particle of polymer with a relatively larger primary particle size, a polymerization method such as soap-free polymerization and fine suspension polymerization can be used. A fine particle of polymer prepared by these methods has a particle size about ten times as large as that by emulsion polymerization using an emulsifier. Soap-free emulsion polymerization as used herein means polymerization characterized in that an emulsifier is not contained during the step of initiation of forming a fine particle of polymer, where once polymer particle formation is initiated, i.e., during the step of particle growing, polymerization may be conducted using an emulsifier.

On the contrary, a polymer having a relatively smaller primary particle size may be prepared by emulsion polymerization using an emulsifier, i.e., a polymerization method characterized in that an emulsifier is contained at the initiation of forming a

fine particle of polymer.

A fine particle of polymer of this invention in which a specific surface area is within a particular range and an oil absorption rate is a particular value
5 or less may be prepared by any of the following methods.

a) During drying a polymer dispersion, a residence time in a drying chamber is extended as much as possible for avoiding rapid drying.

b) During drying a polymer dispersion, a
10 difference between an evaporation temperature of a dispersion medium and an atmosphere temperature in the drying chamber for avoiding rapid drying.

c) During drying a polymer dispersion, a dispersion in which primary particles have a larger
15 particle size is prepared for facilitating evaporation of a dispersion medium and also drying the dispersion at a drying temperature below a glass-transition temperature of the polymer for preventing excessive heat fusion among primary particles.

20 An excessively higher oil absorption rate of a fine particle of polymer may be often caused by the presence of a large hollow structure in the center of a dried polymer particle, which is formed during evaporation of a dispersion medium. According to any
25 of the above methods, formation of such a hollow structure can be prevented.

These methods may be appropriately selected or, if necessary, combined depending on a polymer molecular weight, a glass-transition temperature, particle formation, a particle size, a particle structure and a surface structure, to prepare a fine particle of polymer in which both specific surface area and oil absorption rate are within particular ranges.

Among these, the following method may be preferably conducted as a controllable industrial process for preparation with a higher productivity.

An aqueous dispersion of a polymer having an average primary particle size of 500 nm or more is prepared by soap-free emulsion polymerization or fine suspension polymerization. An average particle size is preferably 10 μm or less.

The dispersion is dried by spray drying under the conditions of an atmospheric temperature of [a polymer glass-transition temperature ($^{\circ}\text{C}$) + 20 $^{\circ}\text{C}$] or less, more preferably the polymer glass-transition temperature or less; and 50 $^{\circ}\text{C}$ or over in a drying chamber.

There is not an explicit academic definition for difference between fine suspension polymerization and suspension polymerization. Generally, suspension polymerization is a technique for obtaining particles with a particle size of 100 μm order, while fine

suspension polymerization is used for obtaining relatively smaller particles with a particle size of about several μm to several tens μm . Differences in preparation include, but not limited to, that

- 5 suspension polymerization uses a relatively smaller amount of a dispersant or dispersion aid and requires no special dispersing apparatuses other than a stirring device while fine suspension polymerization uses a relatively larger amount of a dispersant or dispersing aid or an optimal dispersant selection is needed and a
10 special dispersing apparatus other than a stirring device is often used for make the monomers finer. Examples of a special dispersing apparatus include, but not limited to, homogenizers such as a high-pressure
15 homogenizer and an ultrasonic homogenizer and a porous film such as an SPG film.

Besides a fine particle of polymer and a plasticizer, a plastisol composition of this invention may be combined with an inorganic filler, depending on
20 an application.

An inorganic filler used may be appropriately selected depending on an application; for example, a filler such as calcium carbonate, aluminum hydroxide, perlite, clay, colloidal silica, mica powder, silica
25 sand, diatomaceous earth, kaolin, talc, bentonite, glass powder and aluminum oxide; or a pigment such as

titanium oxide and carbon black. Among these, preferable is, but not limited to, calcium carbonate in the light of universality, a price, handling properties, a specific gravity and availability.

5 As described above, a shear speed applied to a plastisol depends on its processing method. In particular, a shear speed applied to a plastisol is very high in coating by an airless spray and a conventional non-halogenated plastisol exhibits
10 considerably poor processing suitability to an airless spray. Airless spray coating is generally used as the most suitable procedure for applying an undercoat material for endowing antichipping, rust prevention and sound isolation properties to a floor base or wheel
15 house in an automobile or a body sealer applied for endowing water-tightness, airtightness, dust resistant property and damping property to a junction or joint of a steel plate constituting an automobile body.

According to this invention, a non-halogenated
20 plastisol composition can be provided, which is suitable to a processing method in which a higher shear force is applied, such as airless spray coating, and has excellent viscosity properties. It will be described in detail.

25 A non-halogenated plastisol composition which is suitable to a processing method in which a higher shear

force is applied, such as airless spray coating, and has excellent viscosity properties, does not contain a polymer containing halogen atoms such as polyvinyl chloride; is an acrylic plastisol containing a

- 5 particulate acrylic polymer consisting of primary particles with an average particle size of 500 nm or more, a plasticizer and an inorganic filler; and has a viscosity of 0.1 to 1.0 Pa·s (25 °C) as determined with a shear speed of 10000 sec⁻¹ and 100 to 1000 Pa·s (25
10 °C) with a shear speed of 0.42 sec⁻¹.

A plastisol composition of this invention suitable to a processing method in which a higher shear force is applied preferably has a viscosity of 0.1 to 1.0 Pa·s (25 °C) as determined with a shear speed of 10000 sec⁻¹.

- 15 If a viscosity is too high at this shear speed, the composition is highly viscous when a high shear speed is applied by an airless spray so that fine atomization becomes difficult and an even and flat coating surface cannot be provided. If a viscosity is too low at this
20 shear speed, atomized particles are easily spattered under usual conditions for airless spray coating, leading to deteriorated workability in coating. A viscosity at a shear speed of 10000 sec⁻¹ is preferably within a range of 0.1 to 1.0 Pa·s (25 °C), more
25 preferably 0.3 to 0.8 Pa·s (25 °C). A viscosity within such a range is suitable because even coating can be

conducted irrespective of a film thickness and spraying conditions.

Although airless spraying becomes relatively difficult, a viscosity outside of the above range may
5 be used because there are no problems as long as an application method in which a shear speed is relatively low is used.

A plastisol composition of this invention suitable to a processing method in which a higher shear force is
10 applied preferably has a viscosity of 100 to 1000 Pa·s (25 °C) at a shear speed of 0.42 sec⁻¹. If a viscosity is too low at this shear speed, an applied plastisol composition may be sagged so that, for example, an applied film having an adequate film thickness as an
15 antichipping film cannot be formed. On the other hand, if the viscosity is too high, twisting may occur, leading to a deteriorated appearance. A viscosity at a shear speed of 0.42 sec⁻¹ is, therefore, preferably within a range of 100 to 1000 Pa·s (25 °C), more
20 preferably 200 to 600 Pa·s. A viscosity within such a range is suitable because even coating can be conducted irrespective of a film thickness and spraying conditions.

In a plastisol composition of this invention
25 suitable to a processing method in which a higher shear force is applied, a fine particle of polymer is

preferably made of an acrylic polymer such as any of the above acrylic polymers. In particular, a polymer containing 50 mol% or more of an alkyl (meth)acrylate unit is preferable.

5 Furthermore, it is preferable that a fine particle of polymer is made of agglomerates consisting of a plurality of primary particles and that the primary particles constituting such a fine particle of polymer have an average particle size of 500 nm or more as is described above. Primary particles having an average
10 particle size of 500 nm or more may facilitate controlling a specific surface area of the fine particle of polymer within a desired range so that the plastisol can have desired rheology. An average
15 particle size of primary particles is preferably 10 μm or less for achieving quick melting or deposition for a short period.

There are no restrictions to an inorganic filler used in a plastisol composition of this invention
20 suitable to a processing method in which a higher shear force is applied, but the above inorganic fillers and pigments may be used. A combination of inorganic fillers with an average particle size of less than 2.0 μm (C1) and of 2.0 μm or more (C2) in a ratio (by
25 weight) of 30/70 to 70/30 is suitable to a processing method in which a higher shear force is applied.

An inorganic filler with an average particle size of less than 2.0 μm (C1) is effective for increasing a viscosity at a low shear speed and acts as an
antisagging agent. When the ratio (by weight) of the
5 inorganic filler (C1) is within a range of 30/70 to
70/30, sagging can be effectively prevented.
Specifically, a plastisol has a viscosity adequately
low at a high shear speed while being adequately
thixotropic to prevent sagging at a low shear speed.

10 An inorganic filler with an average particle size
of 2.0 μm or more (C2) is effective for reducing a
viscosity at a high shear speed and may improve
suitability to an airless spray. When the ratio (by
weight) of the inorganic filler (C2) is within a range
15 of 30/70 to 70/30, suitability to an airless spray may
be effectively improved.

A configuration as described above may provide a
plastisol composition particularly suitable to a
processing method in which a higher shear force is
20 applied, such as airless spraying.

A plasticizer used in this invention is not
specifically restricted and may be appropriately
selected depending on an application or processing
method of a plastisol. It is preferably a phthalic
25 acid diester of an aliphatic alcohol having 7 to 10
carbon atoms, which is contained in 50 wt% or more of

the total plasticizers because a phthalic acid diester is industrially readily produced, is highly available due to its lower price and therefore carries economic advantages. It has lower boiling point and vapor

5 pressure than those in a phthalic acid diester of an aliphatic alcohol having 6 or less carbon atoms so that volatilization during deposition of a plastisol by heating may be considerably limited. It is more polar and has a lower molecular weight than a phthalic acid
10 diester of an aliphatic alcohol having 11 or more carbon atoms so that it may allow a fine particle of polymer to be properly plasticized during deposition by heating, resulting in improvement of film properties such as strength and elongation. Examples of such a
15 plasticizer include di-2-ethylhexyl phthalate (DOP), di-i-nonyl phthalate (DINP), di-n-nonyl phthalate (DNP) and di-i-decyl phthalate (DIDP).

Other examples of such a plasticizer may be a wide variety compounds; for example, dialkyl phthalates such
20 as di-n-butyl phthalate (DBP), dihexyl phthalate and dioctyl phthalate; alkyl aryl phthalates such as alkyl benzyl phthalates including butyl benzyl phthalate (BBP); diaryl phthalates such as dibenzyl phthalate; dibasic acid esters such as adipates including dibutyl
25 adipate and dioctyl adipate (DOA), dibutyl sebacate and dioctyl sebacate (DOS); triaryl phosphates such as

tricresyl phosphate; trialkyl phosphates; alkyl aryl phosphates; ethers; polyesters; soybean oils such as epoxidated linseed oil and epoxidated soybean oil; citrates such as acetyl tributyl citrate (ATBC);
5 aliphatic acid esters of glycelol; and polyethers.

These may be added depending on physical properties required to a plastisol composition, i.e., features of individual plasticizers such as cold resistance, flame resistance, oil resistance, a low
10 viscosity and low thixotropy.

These plasticizers may be used alone or in combination of two or more depending on a purpose.

A blending proportion of a plasticizer and a fine particle of polymer may be appropriately selected
15 because it may vary depending on an application or processing method of a resulting plastisol composition. Generally, a plasticizer is added preferably 50 to 300 wt parts, more preferably 60 to 200 wt parts, particularly 80 to 200 wt parts per 100 wt parts of a
20 fine particle of polymer in the light of physical properties of a coating film or molding and viscosity properties of a plastisol. A blending proportion of a filler may be also appropriately selected depending on an application or processing method, and for example, a
25 filler may be added in a range of 50 to 400 wt parts per 100 wt parts of a fine particle of polymer.

To a non-halogenated plastisol composition of this invention, a variety of additives may be added as necessary. Examples of such an additive include, but not limited to, diluents such as mineral turpentine and mineral spirit, antifoaming agents, antifungal agents, deodorants, antibacterial agents, surfactants, lubricants, ultraviolet absorbers, perfumes, foaming agents, leveling agents and adhesives.

In some applications, a non-halogenated plastisol composition of this invention may contain a block isocyanate and/or an amino compound containing an amino group having an active hydrogen as an adhesion aid and may be then applied to a cation electrodeposition plate. Such a plastisol containing an adhesion aid may be applied to a cation electrodeposition plate to generate a strong chemical bonding of plastisol film-adhesion aid-cation electrodeposition plate so that a strongly adhered coating film may be formed, resulting in, for example, improvement in antichipping, damping and waterproof properties of the coating film.

A non-halogenated plastisol composition of this invention may be used for producing articles including, but not limited to, various film products and moldings in a wide variety of applications such as wallpapers, undercoats for an automobile, body sealers for an automobile, carpet backing materials, floor materials,

paints and toys.

In particular, this invention can provide, because viscosity properties of a plastisol are controlled, a plastisol composition having excellent processability
5 in coating, sealing, specifically in a body sealer or undercoat for an automobile.

Examples

This invention will be specifically described with reference to Examples.

10 The following evaluation methods are used in Examples.

[Primary particle size]

A primary particle size of a fine particle of polymer was determined using a laser diffraction-
15 diffusion type size distribution measurement device LA-910 (Horiba, Ltd.). In this determination, purified water was used as a dispersing medium and ultrasonication for 2 min was conducted with an ultrasonic generator as an accessory to this device for
20 preventing aggregation of particles.

[Specific surface area]

A specific surface area of a fine particle of polymer was determined using a nitrogen-adsorption type surface area measurement device (Horiba, Ltd.; SA-6200)
25 to calculate a specific surface area per one gram of a fine particle of polymer (unit: m^2/g).

[Oil absorption rate]

An oil absorption rate of a fine particle of polymer (unit: mL/g) was determined by a method described in JIS K-5101.

5 [Minimum plasticizer amount]

A plasticizer (diisononyl phthalate (DINP)) was gradually added to 100 wt parts of a fine particle of polymer and the total amount until the system became flowable was defined as a minimum requirement for forming a plastisol, i.e., a minimum plasticizer amount (unit: phr).

[Determination of a viscosity at a low shear speed]

A plastisol composition obtained was adjusted to 25 °C in a thermostatic bath and was then determined for its viscosity (unit: Pa·s) at a rotating speed of 2 rpm using a Brookfield viscometer (Toki Sangyo Ltd.; BH type viscometer, No.7 rotor), where a shear speed was 0.42 sec⁻¹.

[Storage stability]

20 A plastisol composition obtained was kept at 30 °C in a thermostatic chamber. After one week, the composition was removed from the bath to determine a viscosity. The viscosity measurement and a viscosity immediately after producing the plastisol composition were used to calculate a viscosity-increasing rate (unit: %) for the plastisol according to the following

equation:

(a viscosity after keeping at 30 °C for 1 hour /
an initial viscosity) × 100 (%)

where a viscosity means one at a low shear speed.

5 [Determination of strength of a molding]

A plastisol composition obtained was applied to a
glass plate with a released paper to a thickness of 2
mm. It was molded by heating in an oven at 180 °C for
10 min to form an even film. After peeling, the film
was cut into a No.3 dumbbell shape to give a test piece,
according to a procedure described in JIS K-7113, and
the test piece was measured for a strength of a cured
film (unit: MPa) using a tensilon measuring device
under the conditions of a test speed of 200 mm/min, a
load-cell rating of 980 N and an ambient temperature of
25 °C during measurement.

[Determination of a viscosity at a high shear speed]

A plastisol composition obtained was adjusted to
25 °C in a thermostatic bath and was then measured for
its viscosity using a Herculex high-shear viscometer
(Kumagaya Riki Kogyo Ltd.). Specifically, variation in
a viscosity was determined as a rotation speed was
continuously increased from 0 rpm to 8800 rpm over 30
sec using a C type bob. Although the maximum shear
speed was about 38000 sec⁻¹, a viscosity was read from a
graph of shear speed vs viscosity obtained at the time

of a shear speed of 10000 sec⁻¹.

[Suitability to an airless spray]

Each of the plastisol compositions from Examples and Comparative Examples was applied to a cation electrodeposition plate (a dull steel plate to which an epoxy cationic electrodeposition paint was applied) using an airless spray gun equipped with a nozzle tip GGO-517 (Nippon Gray Ltd.; a tip aperture of 0.432 mm). The coating gun was operated at a distance of about 30 cm from the test plate while being kept perpendicular to the cation electrodeposition plate. A spraying pressure was 13.0 MPa and a temperature was about 25 °C. Suitability to an airless spray was evaluated according to the following ratings.

◎: A sol is sprayed as a fine fume. Good suitability to an airless spray.

○: A fumed sol provides slightly coarse droplets. Moderately good suitability to an airless spray.

△: Spraying is difficult under the above conditions. Suitability to an airless spray is inadequate, but it may be suitably used in a processing method other than an airless spray.

[Antisagging property]

A test plate on which a composition was applied as described above was vertically placed and left for 30 min. It was heated at 140 °C for 20 min to form a film.

Then, the largest film thickness where sagging did not occur in a film (a sagging critical film thickness) was determined. A film thickness measured was evaluated according to the following ratings.

5 ⊙: 4 mm or more. Good antisagging property.

 ○: 2 mm or more to less than 4 mm. Moderately good antisagging property.

 △: less than 2 mm. Antisagging property is inadequate, but it may be suitably used in a processing
10 method other than an airless spray.

[Adhesiveness]

 As described in the above test for suitability to an airless spray, a composition was applied to a film thickness of 1000 μm , and the product was heated at 140
15 °C for 20 min to form a film. The coating test plate was patterned, using a knife, as a matrix of 11 \times 11 parallel lines with 2 mm intervals which reached the metal surface, to form a lattice pattern of scotches such that 10 \times 10 = 100 grids are formed in 4 cm^2 . On
20 the coated surface was firmly attached a cellophane tape, which was then peeled by quickly pulling it. Grids in the plastisol composition film adhering to the cellophane tape which was peeled from the cation electrodeposition plate were counted. Adhesiveness was
25 evaluated from the number of grids peeled from the coating film according to the following ratings.

◎: 10 or less.

○: 11 to 30.

×: 31 or more.

Example 1: Preparation of a fine particle of polymer

5 (A1)

10 In a 5 liter four-necked flask equipped with a thermometer, a nitrogen-gas inlet, a stirrer, a dropping funnel and a reflux condenser was placed 1414 g of purified water, and nitrogen gas was adequately bubbled into the water for 30 min to purge dissolved oxygen in the purified water. After stopping nitrogen gas, 45.6 g of methyl methacrylate and 34.9 g of n-butyl methacrylate were added and the mixture was stirred at 150 rpm while being heated to 80 °C. After 15 the internal temperature became 80 °C, 0.70 g of potassium persulfate dissolved in 28 g of purified water was added at one time to initiate soap-free polymerization. The mixture was stirred at the same temperature, 80 °C, for 60 min to provide a seed 20 particle dispersion.

Then, to the seed particle dispersion was added dropwise a monomer emulsion (prepared by mixing 638.4 g of methyl methacrylate, 487.8 g of n-butyl methacrylate, 9.80 g of sodium dialkylsulfosuccinate (Kao Corporation, 25 Trade name: Perex O-TP) and 490.0 g of purified water and stirring the mixture to give an emulsion) over 3

hours, and the mixture was stirred at 80 °C for additional one hour to provide a polymer dispersion.

Then, to the polymer dispersion was added dropwise a monomer emulsion (prepared by mixing 294.6 g of methyl methacrylate, 179.1 g of i-butyl methacrylate, 14.5 g of methacrylic acid, 4.20 g of sodium dialkylsulfosuccinate (Kao Corporation, Trade name: Perex O-TP) and 210.0 g of purified water and stirring the mixture to give an emulsion) over 1.5 hours, and the mixture was stirred at 80 °C for additional one hour to provide a polymer dispersion.

The resulting polymer dispersion was cooled to room temperature and was spray-dried under the conditions of an inlet temperature of 170 °C, an outlet temperature of 75 °C and an atomizer rotation number of 25000 rpm using a spray drier (Ogawara Kakoki Ltd., L-8 type) to provide a fine particle of polymer (A1).

Example 2: Preparation of a fine particle of polymer (A2)

In a 5 liter four-necked flask equipped with a thermometer, a nitrogen-gas inlet, a stirrer, a dropping funnel and a reflux condenser was placed 720 g of purified water, and nitrogen gas was adequately bubbled into the water for 30 min to purge dissolved oxygen in the purified water. After stopping nitrogen gas, 45.6 g of methyl methacrylate and 34.9 g of n-

butyl methacrylate were added and the mixture was stirred at 150 rpm while being heated to 80 °C. After the internal temperature became 80 °C, 0.70 g of potassium persulfate dissolved in 28 g of purified water was added at one time to initiate soap-free polymerization. The mixture was stirred at the same temperature, 80 °C, for 60 min to provide a seed particle dispersion.

Then, to the seed particle dispersion was added dropwise a monomer emulsion (prepared by mixing 638.4 g of methyl methacrylate, 487.8 g of n-butyl methacrylate, 9.80 g of sodium dialkylsulfosuccinate (Kao Corporation, Trade name: Perex O-TP) and 490.0 g of purified water and stirring the mixture to give an emulsion) over 3 hours, and the mixture was stirred at 80 °C for additional one hour to provide a polymer dispersion.

Then, to the polymer dispersion was added dropwise a monomer emulsion (prepared by mixing 294.6 g of methyl methacrylate, 179.1 g of i-butyl methacrylate, 14.5 g of methacrylic acid, 4.20 g of sodium dialkylsulfosuccinate (Kao Corporation, Trade name: Perex O-TP) and 210.0 g of purified water and stirring the mixture to give an emulsion) over 1.5 hours, and the mixture was stirred at 80 °C for additional one hour to provide a polymer dispersion.

The resulting polymer dispersion was cooled to

room temperature and was spray-dried under the conditions of an inlet temperature of 170 °C, an outlet temperature of 75 °C and an atomizer rotation number of 25000 rpm using a spray drier (Ogawara Kakoki Ltd., L-8 type) to provide a fine particle of polymer (A2).

Example 3: Preparation of a fine particle of polymer (A3)

A mixture of 911.8 g of methyl methacrylate, 696.8 g of n-butyl methacrylate, 28.0 g of sodium dialkylsulfosuccinate and 14.0 g of benzoyl peroxide was subject to micro suspension polymerization using poly(sodium acrylate) as a dispersion stabilizer, at 80 °C with vigorous stirring to provide a polymer dispersion.

The resulting polymer dispersion was cooled to room temperature and was spray-dried under the conditions of an inlet temperature of 170 °C, an outlet temperature of 75 °C and an atomizer rotation number of 25000 rpm using a spray drier (Ogawara Kakoki Ltd., L-8 type) to provide a fine particle of polymer (A3).

Example 4: Preparation of a fine particle of polymer (A4)

In a 5 liter four-necked flask equipped with a thermometer, a nitrogen-gas inlet, a stirrer, a dropping funnel and a reflux condenser was placed 2240 g of purified water, and nitrogen gas was adequately

bubbled into the water for 30 min to purge dissolved oxygen in the purified water. After stopping nitrogen gas, 45.6 g of methyl methacrylate and 34.9 g of n-butyl methacrylate were added and the mixture was
5 stirred at 150 rpm while being heated to 80 °C. After the internal temperature became 80 °C, 0.70 g of potassium persulfate dissolved in 28 g of purified water was added at one time to initiate soap-free polymerization. The mixture was stirred at the same
10 temperature, 80 °C, for 60 min to provide a seed particle dispersion.

Then, to the seed particle dispersion was added dropwise a monomer emulsion (prepared by mixing 638.4 g of methyl methacrylate, 487.8 g of n-butyl methacrylate,
15 9.80 g of sodium dialkylsulfosuccinate (Kao Corporation, Trade name: Perex O-TP) and 490.0 g of purified water and stirring the mixture to give an emulsion) over 3 hours, and the mixture was stirred at 80 °C for additional one hour to provide a polymer dispersion.

20 Then, to the polymer dispersion was added dropwise a monomer emulsion (prepared by mixing 294.6 g of methyl methacrylate, 179.1 g of i-butyl methacrylate, 14.5 g of methacrylic acid, 4.20 g of sodium dialkylsulfosuccinate (Kao Corporation, Trade name:
25 Perex O-TP) and 210.0 g of purified water and stirring the mixture to give an emulsion) over 1.5 hours, and

the mixture was stirred at 80 °C for additional one hour to provide a polymer dispersion.

The resulting polymer dispersion was cooled to room temperature and was spray-dried under the conditions of an inlet temperature of 170 °C, an outlet temperature of 75 °C and an atomizer rotation number of 25000 rpm using a spray drier (Ogawara Kakoki Ltd., L-8 type) to provide a fine particle of polymer (A4).

Example 5: Preparation of a fine particle of polymer

10 (A5)

In a 5 liter four-necked flask equipped with a thermometer, a nitrogen-gas inlet, a stirrer, a dropping funnel and a reflux condenser was placed 1414 g of purified water and 14.0 g of polyoxyethylenenonyl phenyl ether (Kao Corporation, Trade name: Emulgen 920), and nitrogen gas was adequately bubbled into the mixture for 30 min to purge dissolved oxygen in the purified water. After stopping nitrogen gas, 45.6 g of methyl methacrylate and 34.9 g of n-butyl methacrylate were added and the mixture was stirred at 150 rpm while being heated to 80 °C. After the internal temperature became 80 °C, 0.70 g of potassium persulfate dissolved in 28 g of purified water was added at one time to initiate soap-free polymerization. The mixture was stirred at the same temperature, 80 °C, for 60 min to provide a seed particle dispersion.

Then, to the seed particle dispersion was added dropwise a monomer emulsion (prepared by mixing 638.4 g of methyl methacrylate, 487.8 g of n-butyl methacrylate, 9.80 g of sodium dialkylsulfosuccinate (Kao Corporation, Trade name: Perex O-TP) and 490.0 g of purified water and stirring the mixture to give an emulsion) over 3 hours, and the mixture was stirred at 80 °C for additional one hour to provide a polymer dispersion.

Then, to the polymer dispersion was added dropwise a monomer emulsion (prepared by mixing 294.6 g of methyl methacrylate, 179.1 g of i-butyl methacrylate, 14.5 g of methacrylic acid, 4.20 g of sodium dialkylsulfosuccinate (Kao Corporation, Trade name: Perex O-TP) and 210.0 g of purified water and stirring the mixture to give an emulsion) over 1.5 hours, and the mixture was stirred at 80 °C for additional one hour to provide a polymer dispersion.

The resulting polymer dispersion was cooled to room temperature and was spray-dried under the conditions of an inlet temperature of 170 °C, an outlet temperature of 75 °C and an atomizer rotation number of 25000 rpm using a spray drier (Ogawara Kakoki Ltd., L-8 type) to provide a fine particle of polymer (A5).

Example 6: Preparation of a fine particle of polymer (A6)

In a 5 liter four-necked flask equipped with a

thermometer, a nitrogen-gas inlet, a stirrer, a dropping funnel and a reflux condenser was placed 1120 g of purified water, and nitrogen gas was adequately bubbled into the water for 30 min to purge dissolved oxygen in the purified water. After stopping nitrogen gas, 45.6 g of methyl methacrylate and 34.9 g of n-butyl methacrylate were added and the mixture was stirred at 150 rpm while being heated to 80 °C. After the internal temperature became 80 °C, 0.70 g of potassium persulfate dissolved in 28 g of purified water was added at one time to initiate soap-free polymerization. The mixture was stirred at the same temperature, 80 °C, for 60 min to provide a seed particle dispersion.

Then, to the seed particle dispersion was added dropwise a monomer emulsion (prepared by mixing 638.4 g of methyl methacrylate, 487.8 g of n-butyl methacrylate, 9.80 g of sodium dialkylsulfosuccinate (Kao Corporation, Trade name: Perex O-TP) and 490.0 g of purified water and stirring the mixture to give an emulsion) over 3 hours, and the mixture was stirred at 80 °C for additional one hour to provide a polymer dispersion.

Then, to the polymer dispersion was added dropwise a monomer emulsion (prepared by mixing 193.6 g of methyl methacrylate, 218.7 g of styrene, 14.5 g of methacrylic acid, 4.20 g of sodium

Comparative Example 2: Preparation of a fine particle of polymer (A8)

5 In a 5 liter four-necked flask equipped with a thermometer, a nitrogen-gas inlet, a stirrer, a dropping funnel and a reflux condenser was placed 1414 g of purified water and 14.0 g of polyoxyethylenenonyl phenyl ether (Kao Corporation, Trade name: Emulgen 930), and nitrogen gas was adequately bubbled into the mixture for 30 min to purge dissolved oxygen in the
10 purified water. After stopping nitrogen gas, 45.6 g of methyl methacrylate and 34.9 g of n-butyl methacrylate were added and the mixture was stirred at 150 rpm while being heated to 80 °C. After the internal temperature became 80 °C, 0.70 g of potassium persulfate dissolved
15 in 28 g of purified water was added at one time to initiate soap-free polymerization. The mixture was stirred at the same temperature, 80 °C, for 60 min to provide a seed particle dispersion.

Then, to the seed particle dispersion was added
20 dropwise a monomer emulsion (prepared by mixing 638.4 g of methyl methacrylate, 487.8 g of n-butyl methacrylate, 9.80 g of sodium dialkylsulfosuccinate (Kao Corporation, Trade name: Perex O-TP) and 490.0 g of purified water and stirring the mixture to give an emulsion) over 3
25 hours, and the mixture was stirred at 80 °C for additional one hour to provide a polymer dispersion.

Then, to the polymer dispersion was added dropwise a monomer emulsion (prepared by mixing 294.6 g of methyl methacrylate, 179.1 g of i-butyl methacrylate, 14.5 g of methacrylic acid, 4.20 g of sodium

5 dialkylsulfosuccinate (Kao Corporation, Trade name: Perex O-TP) and 210.0 g of purified water and stirring the mixture to give an emulsion) over 1.5 hours, and the mixture was stirred at 80 °C for additional one hour to provide a polymer dispersion.

10 The resulting polymer dispersion was cooled to room temperature and was spray-dried under the conditions of an inlet temperature of 170 °C, an outlet temperature of 75 °C and an atomizer rotation number of 25000 rpm using a spray drier (Ogawara Kakoki Ltd., L-8
15 type) to provide a fine particle of polymer (A8).
Comparative Example 3: Preparation of a fine particle of polymer (A9)

In a 5 liter four-necked flask equipped with a thermometer, a nitrogen-gas inlet, a stirrer, a
20 dropping funnel and a reflux condenser was placed 1414 g of purified water and 28.0 g of sodium mixed aliphatic acid (Kao Corporation, Trade name: Free Mercer), and nitrogen gas was adequately bubbled into the mixture for 30 min to purge dissolved oxygen in the
25 purified water. After stopping nitrogen gas, 45.6 g of methyl methacrylate and 34.9 g of n-butyl methacrylate

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were added and the mixture was stirred at 150 rpm while being heated to 80 °C. After the internal temperature became 80 °C, 0.70 g of potassium persulfate dissolved in 28 g of purified water was added at one time to
5 initiate soap-free polymerization. The mixture was stirred at the same temperature, 80 °C, for 60 min to provide a seed particle dispersion.

Then, to the seed particle dispersion was added dropwise a monomer emulsion (prepared by mixing 638.4 g
10 of methyl methacrylate, 487.8 g of n-butyl methacrylate, 9.80 g of sodium dialkylsulfosuccinate (Kao Corporation, Trade name: Perex O-TP) and 490.0 g of purified water and stirring the mixture to give an emulsion) over 3 hours, and the mixture was stirred at 80 °C for
15 additional one hour to provide a polymer dispersion.

Then, to the polymer dispersion was added dropwise a monomer emulsion (prepared by mixing 294.6 g of methyl methacrylate, 179.1 g of i-butyl methacrylate, 14.5 g of methacrylic acid, 4.20 g of sodium
20 dialkylsulfosuccinate (Kao Corporation, Trade name: Perex O-TP) and 210.0 g of purified water and stirring the mixture to give an emulsion) over 1.5 hours, and the mixture was stirred at 80 °C for additional one hour to provide a polymer dispersion.

25 The resulting polymer dispersion was cooled to room temperature and was spray-dried under the

conditions of an inlet temperature of 170 °C, an outlet temperature of 75 °C and an atomizer rotation number of 25000 rpm using a spray drier (Ogawara Kakoki Ltd., L-8 type) to provide a fine particle of polymer (A9).

5 Comparative Example 4

A commercially available vinyl chloride particulate homopolymer (Nippon Zeon Ltd.) was sieved for classification to provide a fine particle of polymer (A10).

10 Comparative Example 5

A commercially available vinyl chloride/vinyl acetate a particulate copolymer (Nippon Zeon Ltd.) was sieved for classification to provide a fine particle of polymer (A11).

15 Examples 7 to 13: Preparation of fine particles of polymer (A12) to (A18)

Fine particles of polymer (A12) to (A18) were prepared as described for preparation of a fine particle of polymer (A1) except using the compositions shown in Table 1 as a monomer composition.

Table 1 summarizes the compositions of the above fine particles of polymer (A1) to (A18), particle structures, primary particle sizes, specific surface area and oil absorption rates.

25

Polymer No.	Polymer composition (mol%)	Particle Structure	Particle size (μm)	Specific surface area (m ² /g)	Oil absorption rate (mL/g)	Minimum plasticizer amount (phr)
A1	(MMA/nBMA)←-(MMA/iBMA/MAA) 70(65/35)←-30(70/30/4)	Core Shell	0.69	8.1	0.70	75
A2	(MMA/nBMA)←-(MMA/iBMA/MAA) 70(65/35)←-30(70/30/4)	Core Shell	1.45	4.5	0.55	60
A3	MMA/nBMA 65/35	Homogeneous	8.60	0.8	0.62	70
A4	(MMA/nBMA)←-(MMA/iBMA/MAA) 70(65/35)←-30(70/30/4)	Core Shell	0.48	12.1	0.80	90
A5	(MMA/nBMA)←-(MMA/iBMA/MAA) 70(65/35)←-30(70/30/4)	Core Shell	0.29	17.5	1.00	120
A6	(MMA/nBMA)←-(MMA/StMAA) 70(65/35)←-30(46/50/4)	Core Shell	1.10	5.6	0.62	70
A7	MMA/nBMA 65/35	Homogeneous	18.00	0.4	0.40	50
A8	(MMA/nBMA)←-(MMA/iBMA/MAA) 70(65/35)←-30(70/30/4)	Core Shell	0.21	26.0	1.10	130
A9	(MMA/nBMA)←-(MMA/iBMA/MAA) 70(65/35)←-30(70/30/4)	Core Shell	0.10	50.0	1.20	145
A10	VC	Homogeneous	6.30	1.2	0.58	65
A11	VC/VAc	Homogeneous	2.20	2.8	0.55	65
A12	(MMA/nBMA)←-(MMA/iBMA/MAA/HEMA) 50(65/35)←-50(67/29/2/2)	Core Shell	0.60	5.8	0.64	75
A13	(MMA/nBMA)←-(MMA/iBMA/MAA/HEMA) 50(65/35)←-50(67/29/2/2)	Core Shell	1.06	5.7	0.66	75
A14	(MMA/nBMA)←-(MMA/iBMA/MAA/HEMA) 50(65/35)←-50(67/29/2/2)	Core Shell	1.94	6.1	0.65	75
A15	(MMA/nBMA)←-(MMA/iBMA/MAA/HEMA) 50(65/35)←-50(67/29/2/2)	Core Shell	0.36	5.6	0.66	75
A16	(MMA/nBMA)←-(MMA/iBMA/MAA/HEMA) 50(65/35)←-50(67/29/2/2)	Core Shell	0.12	5.6	0.68	75
A17	(MMA/nBMA/AAEM)←-(MMA/iBMA/MAA/AAEM) 50(63/35/2)←-50(67/29/2/2)	Core Shell	1.06	6.2	0.72	80
A18	(MMA/nBMA/GMA)←-(MMA/iBMA) 50(63/35/2)←-50(70/30)	Core Shell	1.06	7.0	0.68	75

In the polymer compositions in Table 1, the symbol " \leftarrow " indicates a core-shell structure. Specifically, compositions of the left and the right sides of the symbol " \leftarrow " are a core and a shell polymers,

5 respectively. A number in parentheses indicates a copolymer composition (mol%) in a core or shell polymer while a number outside of parentheses indicates a component rate (mol%) of a core or shell polymer to the whole core-shell structure particles.

10 Abbreviations in Table 1 have the following meanings.

MMA: methyl methacrylate

nBMA: n-butyl methacrylate

iBMA: i-butyl methacrylate

15 MAA: methacrylic acid

HEMA: 2-hydroxyethyl methacrylate

AAEM: acetoacetoxyethyl methacrylate

GMA: glycidyl methacrylate

St: styrene

20 VC: vinyl chloride

VAc: vinyl acetate.

Example 14: Preparation of a plastisol

To 100 wt parts of the above fine particle of polymer (A1) was added 100 wt parts of diisononyl
25 phthalate (DINP) and the mixture was kneaded at room temperature for 1 min with a homodisper (Tokushu Kika

Industries Ltd., Trade name: TK Homodisper) at about 3000 rpm to provide a homogenous mixture, which was then defoamed in vacuo for 30 min to give a plastisol composition.

- 5 Examples 15 to 35 and Comparative Examples 6 to 10:
Preparation of plastisols

- Plastisol compositions were prepared by mixing a plasticizer and a filler according to Tables 2 and 3 to 100 wt parts of fine particles of polymer (A2 to A18) as described in Example 14. When blending a block isocyanate or polyamide-polyamine, 5 wt part was added to 100 wt parts of a fine particle of polymer and the mixture was again kneaded at about 3000 rpm for 1 min with a homodisper (Tokushu Kika Industries Ltd., Trade name: TK Homodisper) to provide a homogenous mixture, which was then defoamed in vacuo for 30 min to give a plastisol composition.

- Table 2 shows compounding examples of a plastisol consisting of a fine particle of polymer and a plasticizer without a filler, while Table 3 shows compounding examples of a plastisol further comprising another component such as a filler.

Table 2

	Fine particle of polymer	DINP (wt. part)	Presence of halogen atoms	Low shear viscosity (Pa·s)	Storage stability (%)	High shear viscosity (Pa·s)	Strength (MPa)
Ex.14	A1	100	No	8.4	32	-	3.8
Ex.15	A2	100	No	8.3	28	-	3.5
Ex.16	A3	100	No	6.3	17	-	2.8
Ex.17	A4	100	No	17.1	48	-	3.3
Ex.18	A5	100	No	16.5	55	-	3.8
Ex.19	A6	100	No	7.6	33	-	2.7
Comp.Ex.6	A7	100	No	6.5	10	-	0.3
Comp.Ex.7	A8	100	No	82.7	250	-	1.7
Comp.Ex.8	A9	100	No	Over a detection limit	>200	-	1.5
Comp.Ex.9	A10	100	Yes	5.5	17	-	4.8
Comp.Ex.10	A11	100	Yes	5.7	13	-	3.2

Table 3

	Fine particle of polymer	Calcium carbonate			DNP (wt. part)	Block isocyanate	Polyamide-polyamine	Halogen	Low shear viscosity (Pa-s)	Storage stability (%)	High shear viscosity (Pa-s)	Suitability to airless spray	Anti-sagging	Adhesiveness	Strength (MPa)
		Ave. particle size (μm)		Coarse particle											
		(Mix. ratio(%))													
		Fine particle													
Ex. 20	A12	Neolite SP150 0.07(50%)	NS#500 4.44(50%)	140	Yes	Yes	No	370	5	0.55	⊙	⊙	○		2.2
Ex. 21	A13	Neolite SP150 0.07(50%)	NS#500 4.44(50%)	140	Yes	Yes	No	340	4	0.50	⊙	⊙	⊙	○	2.3
Ex. 22	A14	Neolite SP150 0.07(50%)	NS#500 4.44(50%)	140	Yes	Yes	No	280	7	0.49	⊙	⊙	⊙	○	2.1
Ex. 23	A13	Neolite SP150 0.07(100%)	No	160	Yes	Yes	No	585	12	0.28	○	⊙	⊙	○	2.5
Ex. 24	A13	Neolite SP150 0.07(90%)	NS#500 4.44(10%)	140	Yes	Yes	No	452	6	0.83	○	⊙	⊙	○	2.3
Ex. 25	A13	NS#2300 0.97(100%)	No	140	Yes	Yes	No	166	14	0.60	⊙	⊙	○	○	2.8
Ex. 26	A13	Neolite SP150 0.07(50%)	NS#500 4.44(50%)	130	Yes	Yes	No	870	7	0.79	⊙	⊙	⊙	○	2.4
Ex. 27	A13	Neolite SP150 0.07(100%)	No	180	Yes	Yes	No	430	14	0.07	△	△	⊙	○	2.7
Ex. 28	A13	Neolite SP150 0.07(25%)	NS#500 4.44(50%)	140	Yes	Yes	No	152	4	1.30	△	△	○	○	2.1
Ex. 29	A13	No	NS#500 4.44(100%)	140	Yes	Yes	No	20	2	0.89	○	○	△	○	1.9
Ex. 30	A13	Neolite SP150 0.07(50%)	NS#500 4.44(50%)	120	Yes	Yes	No	1750	7	1.35	△	△	⊙	○	2.2
Ex. 31	A15	Neolite SP150 0.07(50%)	NS#500 4.44(50%)	140	Yes	Yes	No	1100	7	0.68	⊙	⊙	⊙	○	2.5
Ex. 32	A16	Neolite SP150 0.07(50%)	NS#500 4.44(50%)	140	Yes	Yes	No	2440	5	1.22	△	△	⊙	○	2.3
Ex. 33	A17	Neolite SP150 0.07(50%)	NS#500 4.44(50%)	140	Yes	No	No	320	4	0.48	⊙	⊙	⊙	⊙	2.4
Ex. 34	A18	Neolite SP150 0.07(50%)	NS#500 4.44(50%)	140	No	Yes	No	340	3	0.58	⊙	⊙	⊙	⊙	2.2
Ex. 35	A17	Neolite SP150 0.07(50%)	NS#500 4.44(50%)	140	No	No	No	300	2	0.46	⊙	⊙	⊙	○	2.1

Abbreviations in Table 3 have the following meanings.

Neolite SP150: Takehara Chemicals Ltd., trade name: Neolite SP 150

5 NS#2300: Nitto Hunka Ltd., trade name: NS#2300

NS#500: Nitto Hunka Ltd., trade name: NS#500

Block isocyanate: Kyoei Chemicals Ltd., trade name: AM-801

Polyamide-polyamine: Fuji Kasei Ltd., trade name: 10 Tomaide 275.

Discussion on Examples 1 (14) and 2 (15)

50 Fine particles of polymer (A1, A2) in Examples 1 and 2 had a specific surface area within a range required in this invention and also an oil absorption 15 rate within a preferable range; contain preferable types of monomer unit; and had a preferable particle structure. Plastisols prepared from these fine particles of polymer (Examples 14 and 15) contained no halogen atoms and of course, articles produced from 20 these also contained no halogen atoms. These fine particles of polymer have a specific surface area and an oil absorption rate within optimum ranges so that the amount of a plasticizer required for compounding may be reduced and a resulting plastisol has an 25 excellent viscosity and excellent storage stability. Furthermore, they had a core-shell particle structure

so that a molding after heating exhibited good strength, resulting in compatibility between workability and processability.

Discussion on Example 3 (16)

5 A fine particle of polymer (A3) in Example 3 had a specific surface area of $0.8 \text{ m}^2/\text{g}$, which was within a range required in this invention. Thus, a resulting plastisol composition (Example 16) exhibited an improved, i.e., low, viscosity and good stability
10 storage. A molding had strength within an adequately practicable range although the strength was slightly lower than those for the moldings (Examples 14 and 15) for the core-shell type fine particles of polymer (A1, A2).

15 Discussion on Example 4 (17)

 A fine particle of polymer (A4) in Example 4 had a specific surface area of 12.1 which was within a range required in this invention. Thus, a resulting plastisol composition (Example 17) exhibited a low
20 viscosity and good stability storage. Since an average particle size of primary particles was $0.48 \text{ }\mu\text{m}$ which is slightly lower than the lower limit of a preferable range, a viscosity was slightly higher than those for the plastisol compositions (Examples 14 and 15) using
25 fine particles of polymer (A1, A2) with an average particle size of primary particles of 500 nm or more.

It was, however, within an adequately practicable range.

Discussion on Example 5 (18)

5 A fine particle of polymer (A5) in Example 5 had a specific surface area of 17.5 which was within a range required in this invention. Thus, a resulting plastisol composition (Example 18) exhibited a low viscosity and good stability storage. Since an oil absorption rate was 1.00 cc/g which was slightly higher than the upper limit of a preferable range, a minimum
10 amount of a plasticizer required for preparing a plastisol was slightly higher, but it was within an adequately practicable range.

Discussion on Example 6 (19)

15 In Example 6, an acrylic monomer was combined with styrene for preparing a polymer, but the resulting fine particle of polymer exhibited a specific surface area, an oil absorption rate and a particle structure within required or preferable ranges in this invention. The resulting plastisol exhibited slightly lower storage
20 stability and strength than those for the plastisols (Examples 14 and 15) using the fine particles of polymer (A1, A2) prepared from an acrylic monomer alone, but they were within adequately practicable ranges.

Discussion on Comparative Example 1 (6)

25 A fine particle of polymer (A7) in Comparative Example 1 prepared by suspension polymerization had a

specific surface area of 0.4 m²/g, which was outside of a range required in this invention. Therefore, although it has an advantage that a plastisol can be prepared with a small amount of a plasticizer, a fine
5 particle of polymer is dissolved too slowly to provide a homogeneous molding in a short period when attempting a molding by heating a resulting plastisol composition (Example 6), leading to a molding with significantly reduced strength. In other words, the plastisol
10 exhibited good workability, but significantly inferior processability.

Discussion on Comparative Examples 2 (7) and 3 (8)

A particulate acrylic polymer having a core-shell structure (A8, A9) in Comparative Examples 2 and 3 had
15 a specific surface area outside of a range required in this invention. In both cases, a minimum amount of a plasticizer required for providing a plastisol was, therefore, very high. Specifically, they were 130 and 145 wt parts in Comparative Examples 2 and 3,
20 respectively. Resulting plastisols (Examples 7 and 8) had a higher viscosity, leading to extremely poor workability.

Discussion on Comparative Examples 4 (9) and 5 (10)

Comparative Examples 4 and 5 used a commercially
25 available polyvinyl chloride. These Examples used a halogen-containing material and therefore, resulting

plastisol compositions (Comparative Examples 9 and 10) contain halogen atoms. They, thus, did not provide a non-halogenated material for which this invention strives. These Comparative Examples were described for
5 performance comparison with this invention.

Discussion on Examples 20 to 35

In all of Examples 20 to 35, a fine particle of polymer with a specific surface area within in a range required in this invention was used and an inorganic
10 filler was added to provide a plastisol composition. Herein, workability in a processing method in which a high shear force is applied by, for example, an airless spray is discussed in detail. The results will be described below.

15 Discussion on Example 20

A plastisol composition in Example 20 contains a fine particle of polymer (A12) with a primary particle size of 600 nm and a 50:50 (by weight) mixture of inorganic fillers with average particle sizes of 0.07
20 μm and 4.44 μm . In this composition, a size distribution of the inorganic filler was within an optimum range and a viscosity of the resulting plastisol composition was also within an optimum range, i.e., 0.55 Pa·s at a high shear speed (10000 sec^{-1}) and
25 370 Pa·s at a low shear speed (0.42 sec^{-1}). It, therefore, exhibited good suitability to an airless

spray to provide a flat coating surface without irregularity and to prevent paint sagging, resulting in a considerably excellent coating film. Furthermore, since the plastisol composition contains a block

5 isocyanate and polyamide-polyamine, adhesiveness to a cation electrodeposition plate was good.

Discussion on Examples 21 and 22

Examples 21 and 22 used fine particles of polymer (A13 and A14) with a primary particle size larger than

10 that in Example 20. The inorganic filler used herein was the same as Example 20 and was blended with the same ratio. In these examples, viscosity values at both high and low shear speeds were within optimum ranges and quite good evaluation results including

15 suitability to an airless spray were obtained. It indicates that a fine particle of polymer with a particle size in such a level may be used to provide good results.

Discussion on Examples 23 and 24

20 Example 23 used the same fine particle of polymer as that in Example 21, but used an inorganic filler only with a smaller particle size and a plasticizer in an increased amount. In this example, a viscosity at a high shear speed was slightly lower than the lower

25 limit of the most preferable range, but was within an adequately preferable range. It gave good results

including suitability to an airless spray.

Example 24 used the same fine particle of polymer as that in Example 21, but a ratio of an inorganic filler was changed. In this example, a viscosity at a high shear speed was slightly higher than the upper limit of the most preferable range, but was within an adequately preferable range. It gave good results including suitability to an airless spray.

Discussion on Examples 25 and 26

Example 25 used the same fine particle of polymer as that in Example 21, but used an inorganic filler with a modified particle size of 0.97 μm alone. In this example, a viscosity at a low shear speed was slightly lower than the lower limit of the most preferable range, but was within an adequately preferable range, giving good results.

Example 26 used the same fine particle of polymer and inorganic filler as those in Example 21, but used a plasticizer in a reduced amount. In this example, a viscosity at a low shear speed was slightly higher than the upper limit of the most preferable range, but was within an adequately preferable range, giving good results.

Discussion on Examples 27 and 28

Example 27 used the same fine particle of polymer and inorganic filler as those in Example 23, but a

plasticizer was considerably increased to 180 wt parts. In this case, a viscosity at a low shear speed was within the optimum range, but a viscosity at a high shear speed was outside of a preferable range. It led to increase in dispersion of the plastisol in an airless spray and thus inferior suitability to an airless spray. It, however, meets the specific surface area condition required in this invention so that it may be satisfactorily used in a processing method other than an airless spray.

Example 28 used the same fine particle of polymer and inorganic filler as those in Example 21, but a blending ratio of the inorganic filler was modified, i.e., the inorganic filler with an average particle size of 2 μm or less was contained only to 25 wt% in the whole inorganic fillers. A viscosity at a low shear speed was, therefore, within a preferable range in this invention while a viscosity at a high shear speed was outside of a preferable range. It was thus difficult to atomize a plastisol composition and to conduct airless spraying. However, it still meets the condition for a specific surface area required in this invention so that it may be suitably used in a processing method other than airless spraying.

Discussion on Examples 29 and 30

Example 29 used the same fine particle of polymer

as Example 21, but used an inorganic filler with an average particle size of 4.44 μm alone. In this example, a viscosity at a high shear speed was within a preferable range, but a viscosity at a low shear speed was so low that it exhibited slightly inferior
5 antisagging property and a slightly disturbed coating-film pattern. It, however, meets the specific surface area condition required in this invention so that it may be satisfactorily used in a processing method other
10 than an airless spray.

Example 30 used the same fine particle of polymer and inorganic filler as Example 21, but the amount of a plasticizer was reduced to 120 wt parts. In this
15 example, both viscosity values at low and high shear speeds were outside of preferable ranges so that airless spraying could not be conducted. It, however, meets the specific surface area condition required in this invention so that it may be satisfactorily used in a processing method other than an airless spray.

20 Discussion on Examples 31 and 32

Examples 31 and 32 used the same filler as Example 20 and reduced the primary particle size of the fine particle of polymer. In both examples, the primary particle size of the fine particle of polymer was
25 outside of a preferable range (500 nm or more), leading to a very high viscosity at a low shear speed. In

particular, the primary particle size of the fine particle of polymer was extremely small in Example 32 so that a viscosity at a high shear speed became too high to conduct airless spraying. They, however, meet
5 the specific surface area condition required in this invention so that they may be satisfactorily used in a processing method other than an airless spray.

Discussion on Examples 33, 34 and 35

Example 33 used the same fine particle of polymer
10 (A12) as Example 20 and Examples 34 and 35 used a fine particle of polymer containing an epoxy group (A18) and an acetacetyl group (A17), respectively. Furthermore, in these examples, blending conditions for a block isocyanate and polyamide-polyamine as adhesion aids
15 were modified. For an inorganic filler, the same conditions as Example 20 were used. In Example 33 or 34, either a block isocyanate or polyamide-polyamine was blended so that improved adhesiveness was achieved by bonding between the functional group in a fine
20 particle of polymer and the functional group on a cation electrodeposition plate. In Example 35, either a block isocyanate or polyamide-polyamine was not blended so that adhesiveness was slightly lower than Examples 33 and 34, but the functional group in the
25 polymer contributed to provide adequate adhesiveness.

CLAIMS

1. A fine particle of polymer for a plastisol free from halogen atoms and having a specific surface area of 0.6 to 20.0 m²/g as determined by nitrogen-gas adsorption.

2. The fine particle of polymer for a plastisol as claimed in Claim 1 wherein an oil absorption rate by linseed oil is 0.8 mL/g or less.

3. The fine particle of polymer for a plastisol as claimed in Claim 1 or 2 wherein the fine particle of polymer is made of an acrylic polymer.

4. The fine particle of polymer for a plastisol as claimed in Claim 1, 2 or 3 wherein the fine particle of polymer has two or more polymer layers having different compositions concentrically from the particle center to its surface.

5 5. The fine particle of polymer for a plastisol as claimed in any of Claims 1 to 4 consisting of agglomerates formed from a plurality of primary particles wherein the primary particles have an average particle size of at least 500 nm.

6. A process for manufacturing the fine particle of polymer for a plastisol as claimed in Claim 5, comprising the steps of:

5 preparing an aqueous dispersion of a fine particle of polymer in which primary particles have an

average particle size of at least 500 nm; and

drying the aqueous dispersion at not lower than 50 °C but not higher than [a glass-transition temperature of the polymer + 20] °C, by spray drying.

7. A non-halogenated plastisol composition comprising the fine particle of polymer for a plastisol as claimed in any of Claims 1 to 5 and a plasticizer.

8. A non-halogenated plastisol composition comprising the particulate acrylic polymer for a plastisol as claimed in any of Claim 5, a plasticizer and an inorganic filler.

9. The non-halogenated plastisol composition as claimed in Claim 8 wherein viscosity values at shear speeds of 10000 sec⁻¹ and 0.42 sec⁻¹ are 0.1 to 1.0 Pa·s (25 °C) and 100 to 1000 Pa·s (25 °C), respectively.

10. The non-halogenated plastisol composition as claimed in Claim 9 wherein the inorganic filler essentially consists of inorganic fillers with an average particle size of less than 2.0 μm (C1) and of 2.0 μm or more (C2) and a component ratio of these inorganic fillers (C1) to (C2) (by weight) is 30/70 to 70/30.

11. The non-halogenated plastisol composition as claimed in any of Claims 7 to 10 wherein the plasticizer comprises a phthalic acid diester of an aliphatic alcohol having 7 to 10 carbon atoms in at

least 50 wt%.

12. A coating material consisting of the plastisol composition as claimed in any of Claims 7 to 11.

13. A sealant consisting of the plastisol composition as claimed in any of Claims 7 to 11.

14. A sealant for an automobile consisting of the plastisol composition as claimed in any of Claims 7 to 11.

15. An undercoating material for an automobile consisting of the plastisol composition as claimed in any of Claims 7 to 11.

16. An article produced using the plastisol composition as claimed in any of Claims 7 to 11.

Japanese Language Declaration
(日本語宣言書)

私は、米国法典第35編119条 (a) - (d) 項又は365条 (b) 項に基づき下記の、米国外の国の少なくとも一カ国を指定している特許協力条約365 (a) 項に基づく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している、本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

Prior Foreign Application(s)
外国での先行出願

11-265280	Japan
(Number)	(Country)
(番号)	(国名)
11-269936	Japan
(Number)	(Country)
(番号)	(国名)

I hereby claim foreign priority under Title 35, United States Code, Section 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority Claimed
優先権主張

20/September/1999	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Day/Month/Year Filed)	Yes	No
(出願年月日)	はい	いいえ
24/September/1999	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Day/Month/Year Filed)	Yes	No
(出願年月日)	はい	いいえ

私は、第35編米国法典119条 (e) 項に基づいて下記の米国特許出願規定に記載された権利をここに主張いたします。

(Application No.)	(Filing Date)
(出願番号)	(出願日)

私は、下記の米国法典第35編120条に基づいて下記の米国特許出願に記載された権利、又は米国を指定している特許協力条約365条 (c) に基づく権利をここに主張します。また、本出願の各請求範囲の内容が米国法典第35編112条第1項又は特許協力条約で規定された方法で先行する米国特許出願に開示されていない限り、その先行米国出願書提出日以降で本出願書の日本国内または特許協力条約国際提出日までの期間中に入手された、連邦規則法典第37編1条56項で定義された特許資格の有無に関する重要な情報について開示義務があることを認識しています。

(Application No.)	(Filing Date)
(出願番号)	(出願日)

(Application No.)	(Filing Date)
(出願番号)	(出願日)

私は、私自信の知識に基づいて本宣言書で私が行なう表明が真実であり、かつ私の入手した情報と私の信じているところに基づく表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第18編第1001条に基づき、罰金または拘禁、もしくはその両方により処罰されること、そしてそのような故意による虚偽の声明を行えば、出願した、又は既に許可された特許の有効性が失われることを認識し、よってここに上記のごとく宣誓を致します。

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application No.)	(Filing Date)
(出願番号)	(出願日)

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code Section 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of application.

(Status: Patented, Pending, Abandoned)
(現況：特許許可済、係属中、放棄済)

(Status: Patented, Pending, Abandoned)
(現況：特許許可済、係属中、放棄済)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Declaration and Power of Attorney For Patent Application

特許出願宣言書及び委任状

Japanese Language Declaration

日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者（下記の名称が複数の場合）であると信じています。

上記発明の明細書は、

☐ 本書に添付されています。

☒ ____月 ____日に提出され、米国出願番号または特許協定条約国際出願番号を____とし、
(該当する場合) ____に訂正されました。

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

私は、連邦規則法典第37編第1条56項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled.

Fine particle of polymer for plastisol and
manufacturing process therefor as well as
non-halogenated plastisol composition and
article produced therefrom

the specification of which

☒ is attached hereto.

☒ was filed on September 20, 2000
as United States Application Number or
PCT International Application Number
PCT/JP00/06408 and was amended on
____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

Japanese Language Declaration
(日本語宣言書)

委任状：私は下記の発明者として、本出願に関する一切の手続きを米特許商標局に対して遂行する弁理士または代理人として、下記の者を指名いたします。
(弁理士、または代理人の指名及び登録番号を明記のこと)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: (list name and registration number)



022850

書類送付先

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発明者の署名	日付	Inventor's signature Toshihiro Kasai Date October 5, 2001
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国籍		Citizenship Japanese
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第二の共同発明者の氏名	2-00	Full name of second joint inventor, if any Toru TSUCHIHASHI
第二の共同発明者の署名	日付	Second joint Inventor's signature Toru Tsuchihashi Date October 5, 2001
住所		Residence Aichi, Japan JPX
国籍		Citizenship Japanese
郵便の宛先		Post Office Address c/o Products Development Laboratories, Mitsubishi Rayon Co., Ltd., 1-60, Sunadabashi 4-chome, Higashi-ku, Nagoya-shi, Aichi 461-8677 Japan

(第三以降の共同発明者についても同様に記載し、署名すること)

(Supply similar information and signature for third and subsequent joint inventors.)